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Thermal Initiation of Methylmethacrylate by Methoxy–oxo-bis [N-(4-bromophenyl) Salicylideneiminato] Vanadium (V)

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Abstract

Methoxy – oxo - bis [N - (4-bromophenyl) Salicylidene – iminato] Vanadium (V) : [VO (Br C_6 H_4 N : C H O C_6 H_4 $)_2$ OCH_3 can initiate methylmethacrylate thermally at 80°C . Under the experimental conditions employed, no retardation or inhibition is observed. The order with respect to the initiator concentration is (0.5), while the order with respect to monomer concentration is (1.8) which gives an indication that the rate of initiation is dependent on monomer concentration.

Spectroscopic studies suggest that during the thermal polymerization a reduction in the oxidation state of vanadium occurs with heterolytic scission of the V- OCH_3 bond and this might be induced by MMA molecule which forms intermediate complex between VOL_2 OCH_3 and methyl methacrylate monomer before the formation of the primary radical responsible for the initiation process.

Activation energies of polymerization as well as initiation processes in the present system were also determined . The tacticity of polymer produced is examined.

According to the experimental results obtained a mechanism of thermal initiation reaction is proposed.

الابتداء الحراري لبلمرة المثيل ميثاكريليت بواسطة ميثوكسي ــ اوكسو ــ ثنائي (N-(٤ - بروموفنيل) سالسيدين امنيتو) فناديوم (٥)

الخلاصة

وجد إن المعقد ميثوكسي – اوكسو – ثنائي (N – (٤ -بروموفنيل) سالسدين امنيتو) فناديوم(٥) يستطيع البدء الحراري لبلمرة المثيل ميثا اكريليت بدرجة ٨٠°م. في البلمرة الحرارية بهذا البادئ وتحت ظروف البلمرة لم يحصل إعاقة أو منع وان رتبة التفاعل بالنسبة لتركيز البادئ هو (٠,٥) بينما كانت الرتبة (١,٨)بالنسبة لتركيز المونيمر وهذا يعطي دلالة على أن سرعة البلمرة تعتمد على تركيز المونيمر. اثبتت من الدراسات الطيفية انه خلال عملية التسخين يحدث اختزال للفناديوم من الحالة الخماسية إلى الحالة الرباعية مع انشطار لإصرة $V\text{-}OCH_3$ الذي يحصل بفعل جزيئة المثيل ميثاكريليت التي تكون مركب وسطي معقد من VOL_2 OCH_3 وجزيئة المثيل ميثاكريليت الذي يكون لاحقا الجذر الحر الأولي المسؤول عن عملية الابتداء.

تم تعيين طاقة تنشيط البلمرة والابتداء لنظام البلمرة الحالي كما تم تشخيص الهيئة الفراغية للبولي مثيل ميثاكريليت الناتج من البلمرة كما واخيراً تم اقتراح ميكانيكية التجزئة الحرارية استنادا إلى النتائج التجريبية التي تم الحصول عليها.

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Introduction

In the last decades,a considerable attention has focused on thermal initiation of vinyl polymerization by transition metal chelates. (1-2)

It was first pointed out by Arnett and Mendelsohn(3) · that these metal chelates have the ability to produce free radicals on heating.

Several transition metal acetylacetonate complexes proved to be a good thermal initiators of styrene polymerization at 110˚C(4)

Kasting and co – workers(5) and Nishikawa and co – workers (6) reported that among simple acetylacetonate , those of Mn^{III} and Co^{III} are the most active initiators in benzene solution at 80˚C.

The mechanism of thermal initiation of styrene , methyl methacrylate (MMA), and acrylonitrile (AN) by Mn^{III} $(acac)_3$ and Mn^{III} $(facac)_3$ complexes, were studied in detail by Bamford and Lind (7) . On the other hand, Indicator and Linder (8) reported that Cu^{II}, Co^{II} and $Fe^{III}(acac)_3$ enhanced the polymerization of MMA in the presence of t – butyl hydroperoxide. Also the polymerization of MMA by cyclic ether hydro peroxide – transition metal acetylacetonates at 50˚C was studied (9) · Co^{III} $(acac)_3$ and Fe^{III} $(acac)_3$ were proved to be effective thermal initiators for styrene and MMA polymerization, respectively(10,11)

Bamford and co – workers (12) reported that Cu^{II} $(acac)_2$ in conjunction with ammonium tichloroactate initiates the polymerization of MMA at 80˚C via free radical mechanism.

The mechanism of free radical polymerization of styrene by Cu^{II} bis – ephidrin CCl_4 ; two component system ; was also reported by Barton and Lazar (13). Uehara and co – workers (14) studied the free radical polymerization of styrene, MMA and vinyl acetate at 70˚C initiated by Mn^{III} $(acac)_3$ in presence of pyridine derivatives as electron doners.It was observed that at 25˚C, free radical polymerization of acrylonitrile in dimethyl sulphoxide solution (DMSO) is readily brought by Mn^{III} $(acac)_3$ chelate complex(15). A mechanistic study of vinyl polymerization by Cu^{II} (1,3 – diaminopropane) / CCl_4 in DMSO solution was demonstrated by Kimura, lanki and Takemoto(16). Thiagarajan and co – workers(17) studied the thermal polymerization of MMA at 70˚C - 80˚C by N,N′, ethylene bis (salicydieneiminato) (bnzoyl – acetylacetonate) cobalt (Щ).

A new type of metal chelate complex { $VO (S_2 CN (R)_2)_3$}, was investigated as a photoinitiators as well as thermal initiators of styrene polymerization at a temperature ranging between 60 -80ºC(18). Saleh and Aliwi (19) have investigated a noval type of metal chelate complex chloro – oxo – bis [N – (4-bromophenyl) salicylideneiminato] Vanadium (V) VO ($Br C_6 H_4 N : CHO C_6 H_4)_2 Cl$) as photoinitiator of styrene polymerization . This initiator proves to be effective thermal initiator of styrene polymerization at 80˚C .

Thermal polymerization of MMA by Manganese (Щ) dithiocarbamate complexes was studied by Aliwi and Al-Hayali(20). The same authores also studied the thermal initiation of MMA by Manganese (Щ) dithiocarbamates in presence of electron donores . (21)

Recently Siemeling and co-workers have investigated complexes with two different types modified imido and phosphaneiminato ligands, these complexes are used for the co-polymerization of the polar olefins: MMA, AN ,and vinyl acetate$^{(22)}$..

Manmeekaur and Srivastava have studied the thermal initiation of MMA bycertain transition metal chelates$^{(23)}$.

Very recently Saleh$^{(24)}$ studied the thermal polymerization of MMA at 80˚C by Chloro – oxo – bis [N – (4-bromophenyl) salicylideneiminato] Vanadium (V) VO (Br C_6 H_4 N = CHO C_6 $H_4)_2$ Cl)chelate complex.

In the present work we have studied the thermal polymerization of MMA at 80˚C by a noval type of metal chelate complex : Methoxy–oxo – bis [N – (4-bromophenyl) salicylideneiminato] Vanadium (V) VO (Br C_6 H_4 N : CHO C_6 $H_4)_2$ OCH_3)chelate complex.

2- Experimental

2-1- Materials

Methoxy– oxo – bis [N – (4-bromophenyl) salicylideneiminato] Vanadium (V) {VO (Br C_6 H_4 N : CHO C_6 $H_4)_2$ OCH_3)}chelate complex.

[VOL_2 OCH_3] was synthesized in two steps , the first involves the conversion of liquid ($VOCl_3$) to {VO(OR) $_3$} derivatives using a method similar to that described by Carten and Caughtan $^{(25)}$. In the second step , the VO(OCH_3) was converted to the complex [VOL_2 OCH_3] adopting the procedure reported by Mookerjee and co-workers$^{(26)}$. .Methyl –methacrylate (MMA) monomer (B.D.H.Ltd) purified as described by Bamford and Lind$^{(7)}$. Analar benzene (B.D.H.Ltd) was dired before distillation. Analar methanol (B.D.H.Ltd.) was used without further purification.

2-2- Technique

Pyrex tube 15 cm, in length, 1.5 cm in diameter, 10 cm^3 capacity was used in polymerization process . The tube was connected to an argon gas purging system in order to remove the dissolved air, bubbling MMA$^{(27)}$ with saturated argon gas (purity 99.96%) for 20 minutes. The reaction tube was protected from light using aluminum foil and placed in a bath at 80˚C ± 1˚C using 150 Watt aquarium heater used in conjunction with Sunvic-Mercury relay switch.

Average rates of polymerization were measured gravimetrically by precipitation of the polymer in 50 fold of pure methanol, and the rate of polymerization was calculated as follows:-

$$w = -\frac{d[M]}{dt} = \frac{[Mo]}{100} \times \frac{\%Conv.}{t} \qquad (1)$$

where: [Mo]= is the initial monomer concentration, conv. % = is the percentage of conversion of monomer to polymer.

t = time of reaction (in second)

The number average molecular weight of polymer (PMMA) was generally determined viscometrically in benzene at 30˚C using Mark-Houwink equation$^{(28)}$.Values of K and ∝ were taken from reference(28).

Infra-red spectra were recorded with a Pye-Unicam SP3-100. IR-spectrophotometer using KBr disk technique. Hitachi U- 2000 double beam UV-visible spectrophotometer was used to measure the changes in initiator concentration and spectra during the polymerization process.

3- Results and discussion.

3-1- Kinetics of thermal initiation.

Figure.(1) illustrates the average rate of polymerization is proportional to the sequare root of the chelate concentration at constant monomer concentration (bulk) and temperature, the straight line in fig.(1) gives the following relation:-

$$\omega = 0.5\mathrm{x}10^{-2}[VOL_2Cl]^{1/2} \qquad \ldots(2)$$

Results shown in Fig.(1)and equation (2) illustrate that no inhibition or retardation is observed in the present initiating system, and the polymerization is considered to be a simple free-radical polymerization. Inhibition and retardation were further checked by determining the percent conversion of monomer to polymer with polymerization time of heating at 80˚C, no inhibition period was detected.(17).

Fig. (2) shows the relationship between percent conversion of monomer to polymer with time of heating at 80˚C.Results shown in Fig.(2) reflect that both inhibition and retardation do not exist in the present polymerization system under the conditions employed.

The slope of the logarithmic plot of the relation between the rate of polymerization and the initiator concentration is equal to (0.5) which indicates the order with respect to initiator concentration is (0.5).Again this also reflects and proves the free radical nature of polymerization process. This result agrees well with that obtained by Arnett(29), Bamford and Lind (7), Aliwi (30), Thiagarajan and co-workers(17) in polymerization of MMA by Azobisisobutyronitrile (AIBN), Mn (acac)$_3$ and VO (acac)$_2$ Cl, and CoSalenBa respectively.

The kinetic parameter $k_p \big/ k_t^{1/2}$ (k_p & k_t) being rate constants of propagation and second order termination respectively. This parameter was calculated from the following relation (30)

$$\left[k_p/k_t^{1/2}\right] = \frac{1}{[M]}\left[\omega D_p \frac{(2+y)}{2(1+y)}\right]^{1/2} \qquad (3)$$

y = ratio of $\frac{ktc}{ktd}$ ktc = termination constant by combination

ktd = termination constant by disproportionation

y=0.77 at 80˚C (31) . Mean value of $k_p \big/ k_t^{1/2}$ was found to be equal to 0.1 $mol^{-1/2}\,\mathrm{l}^{1/2}s^{-1/2}$ This value of $k_p \big/ k_t^{1/2}$ for this initiator is close to from that obtained by Arentt(29) (0.109) $mol^{-1/2}\,\mathrm{l}^{1/2}s^{-1/2}$ for the polymerization of MMA at 77˚C using AIBN as initiator and Bamford & Lind(7) (0.17) and Thiagarajan and co-workers(17). (0.174) $mol^{-1/2}\,\mathrm{l}^{1/2}s^{-1/2}$.

Rate of initiation (υ_i) in bulk MMA at 80°C ; which can be calculated by using equation (4) and calculated value of $k_p \big/ k_t^{1/2}$ can be calculated.

$$W = k_p \big/ k_t^{1/2}[M]^{1/2} \qquad (4)$$

In order to find the rate of polymerization of methymethacrylate with respect to monomer concentration the rate of polymerization was determined at constant temperature (80°C), constant chelate concentration 5×10^{-5} mol .l^{-1} and variable monomer concentration [M] with benzene as diluent.

Figure(3). reveals that order in monomer is (1.8) Thus, the rate of polymerization with respect to monomer is greater than unity (close to two).Thus it is concluded that a monomer molecule is involved in initiation step.This kinetic order of monomer is higher than that of normal equation of vinyl polymerization by radical mechanism it was also observed for the polymerization of styrene and MMA.by several authores. This result is in good agreement with result obtained by Uehera and co-workers(32); obtained an order of 1.5 for the thermal polymerization of styrene by Cu^{Π} $(acac)_2$ complex at 80°C. Prabha and Nandi(11) obtained an order of (1.5) for thermal polymerization of MMA at 70˚C. Bamford and Lind(7) also reported that the order of MMA is(1.5) by Mn $(acac)_3$ at 80˚C. The same authors obtained an order of (1.5) for the thermal polymerization of styrene in benzene and (1.2) in ethyl acetate when thermally initiated at 80˚C using Mn $(acac)_3$ complex. Thiagarajan and co-workers(17) also obtained the order of (1.44) for the polymerization of MMA by CoSalenBa at 80˚C. All these authores suggested that complex formation between the chelate and monomer undergoes a thermal oxidation-reduction reaction.

In order to confirm that the obtained value of (1.8) arises from the kinetic of polymerization and not from other side effects, MMA was polymerized using (AIBN)(29) as thermal initiator at 77˚C. The order with respect to monomer was one which agrees with literature (7), thus it can be concluded that the value of (1.8) arises from the kinetic of polymerization catalyzed by VOL_2OCH_3 . It is clear that initiation process by this initiator depends on monomer concentration. Thus the mechanism of initiation process by this initiator in thermal polymerization is quite different from that of photo initiation process,(the order of monomer is unity), which means the rate of initiation is dependent on monomer concentration.

3.2 Spectral observation

The UV-visible absorption spectrum of VOL_2 OCH_3 ; VO (B_r C_6 H_4 N : CHO C_6 H_4 $)_2$ OCH_3 in MMA solution is shown in Fig (4). On heating at 80˚C the colour of the solution changes gradually from greenish yellow to yellow and the absorption spectrum changes as shown in Fig. (4) and ultimately becomes indistinguishable from that of VOL_2, [VO (B_r C_6 H_4 N: CHO C_6 $H_4)_2$] in MMA.

The appearance of isosebestic points at (385) and (500)nm indicates that the overall chemical changes are relatively simple. It is also noticed that there is little increase in the absorption intensity in the range between (450-800) nm during the heating proess. The very broad low intensity peak may be attributed to d-d electron transition of Vanadium (IV) complexes (33-34).

Infrared absorption spectrum was recorded for the thermal product of the chelate after about (30) hours of heating at 80˚C in benzene saturated solution. The location of the vanadyl group (V = O) stretching vibration wave number before and after heating was monitored which appears at (975) and (980) cm^{-1} respectively. Moreover the V=O stretching vibration of VOL_2 complex prepared as described by Pilienko and co - workers(32) is located at 982 cm^{-1} which is very close to that for V=O stretching in the complex produced upon prolonged heating of the original chelate . Similar shift of V = O stretching vibration to a higher frequency has been observed for photoreduction of V(V) to V (IV) complex(30, 35).

All the spectral observations together with kinetics data obtained therefore, indicate that the primary process in thermolysis is scission of (V- OCH_3) bond and this might be induced by MMA molecule which can form an intermediate complex (I) between vanadium chelate and MMA monomer before the formation of the primany initiating radical

The reaction scheme(1) might be suggested for the generation of the initiating species.

Thus the primary step is therefore heterolytic rather than homolytic (suggested for the photoinitiation mechanism)(36).

3-3 The activation energy for overall polymerization process .

3-3-1 Total activation energy

Figure.(5) shows the Arrehinus plot of MMA / VOL_2 OCH_3 initiating system at 80˚C with reciprocal absolute temperature. The activation energy for overall polymerization process was deduced from the slope of this plot. It was found to be equal to 10.2 kcal. mol^{-1}- This value is close to these reported for thermal polymerization of MMA by Mn $(tfac)_3$ as initiator (7) (E_T = 12.5 kcal mol^{-1}), $Mn(PPd)_3$ (E_T = 11.0 kcal. mol^{-1}) and CoSalenAa (17) as Initiator (E_T = 10.9 kcal mol^{-1})and CoSalenBa. as thermal initiator (17) (E_T = 7.3 kcal. mol^{-1}) .

3-3-2 The activation energy for initiation

The activation energy for initiation could be obtained from activation energy for overall polymerization process using the relation(7).

$$E_T = E_P - \frac{E_t}{2} + \frac{E_i}{2} \qquad \textbf{(5)}$$

where

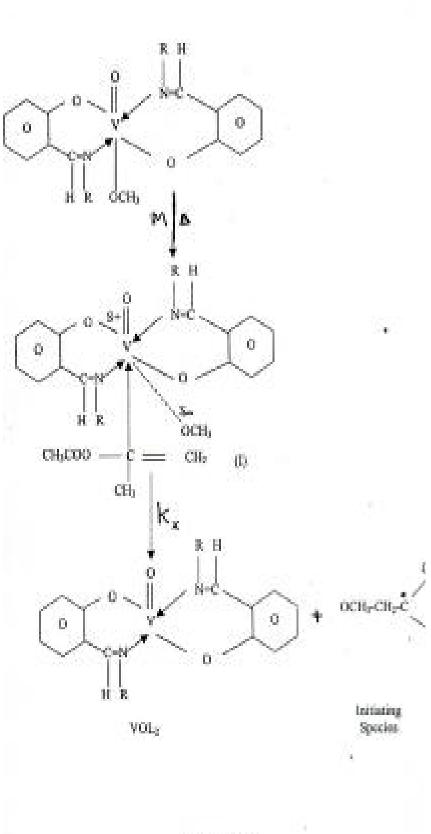
E_i = activation energy of initiation
E_t = activation energy of termination
E_p = activation energy of propagation

The value of $E_p - \frac{E_t}{2}$ is reported in the literature(37) for the polymerization of MMA at 80˚C equal to 4.6 kcal mol^{-1}. Form this value and the value of E_T then E_i is deduced and found to be 15.35 kcal. mol^{-1}.

This value agrees well with that abtained, for Mn $(tfac)_3$ E_i = 15.8 kcal. mol^{-1}, and for Mn $(PPd)_3$ E_i = 12.9 kcal. $mol^{-1(7)}$. Thinagarajan(17) and et.al on the other hand obtained the value of E_i = 11.0 kcal. mol^{-1}. When he used CoSalenAa as thermal initiator and E_i = 3.8 kcal. mol^{-1}. When he used CoSalenBa as initiator.

Detection of polymer tacticity

The tacticty of PMMA produced by the present initiating system was examined by infrared spectroscopy. The IR-spectrum of polymer film is similar to that reported for atactic PMMA(38) and it is quite different from that of isotactic PMMA or syndiotactic PMMA. Thus it is concluded that the radical species is completely detached before the initiation process and the rest of coordination vanadium complex is not involved in the initiation step or propagation process. Therfore there is no chance of any stereoregularity of the MMA repeating units in the polymer chain.



Scheme (1)

Conclusion

The present chelate complex of VOL_2OCH_3 Methoxy-oxo-bis [N-(4-bromophenyl) salicylideneiminato] Vanadium (V) proves to be a novel thermal initiator for the polymerization of MMA at 80˚C, without retardation or inhibition, through free radical mechanism. The order with thermolysis process and formation of primary initiating species regard to initiator is (0.5) while the order of monomer is higher than unity (1.8), which led to suggestion of complex formation between MMA and initiator molecules from which the primary initiating radicals are formed, the latter is responsible for the initiation process.

Kinetic and spectroscopic observations suggest that thermal redox- reaction occur in the complex leads to the reduction of V (V) to V (lV) and this is enhanced by MMA molecule. The PMMA produced by the present initiating system is atactic and thus it has been concluded that the complex molecule is neither involved in initiation nor in propagation steps.

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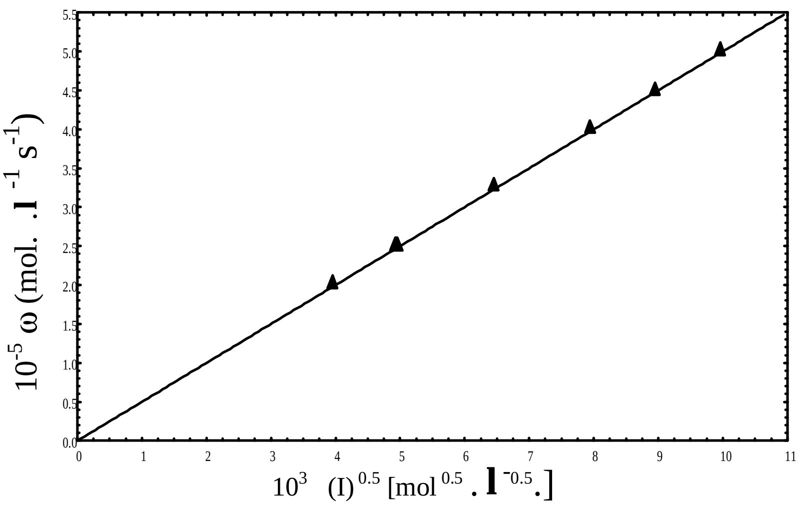


Fig.(1): Dependence of average rate of MMA polymerization (bulk) on the square root of chelate conc.at 80°C. [M] = 9.4 mol. l^{-1}.

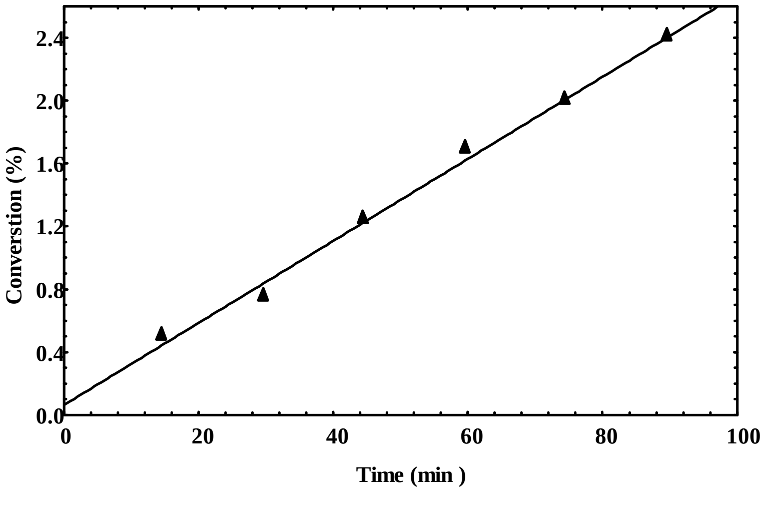


Fig.(2): Relation between % conv. of monomer to polymer and time of heating at 80˚C [I] = 4×10^{-4} mol. l^{-1}.

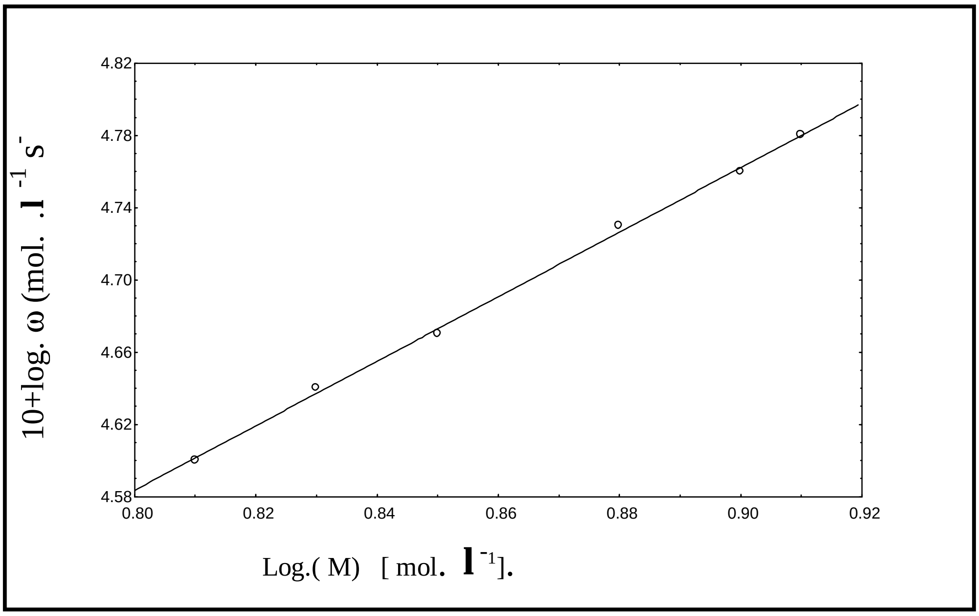
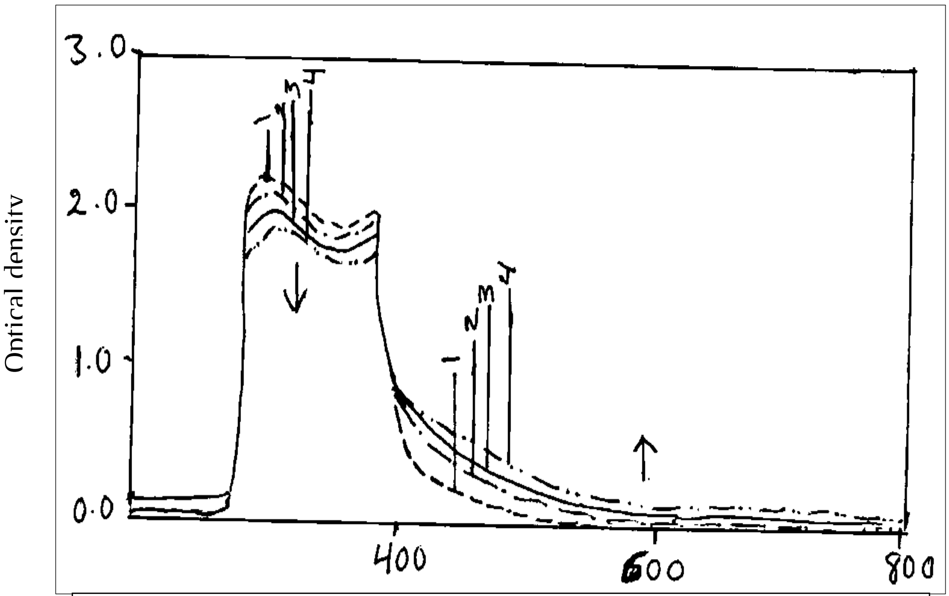


Fig.(3): Rate of Polymerization at 80^0Cof MMA as a function of monomer concentration (benzene is used as diluent).



wave length (nm.)

Fig.(4): UV-visible spectrum of VOL_2OCH_3 in MMA ($5*10^{-5}$) mol . l^{-1}.
1 -Before heating 2-After heating 5min.at 80^0C.
3- After heating 15min.at 80^0C 4- After heating 30min.at 80^0C.

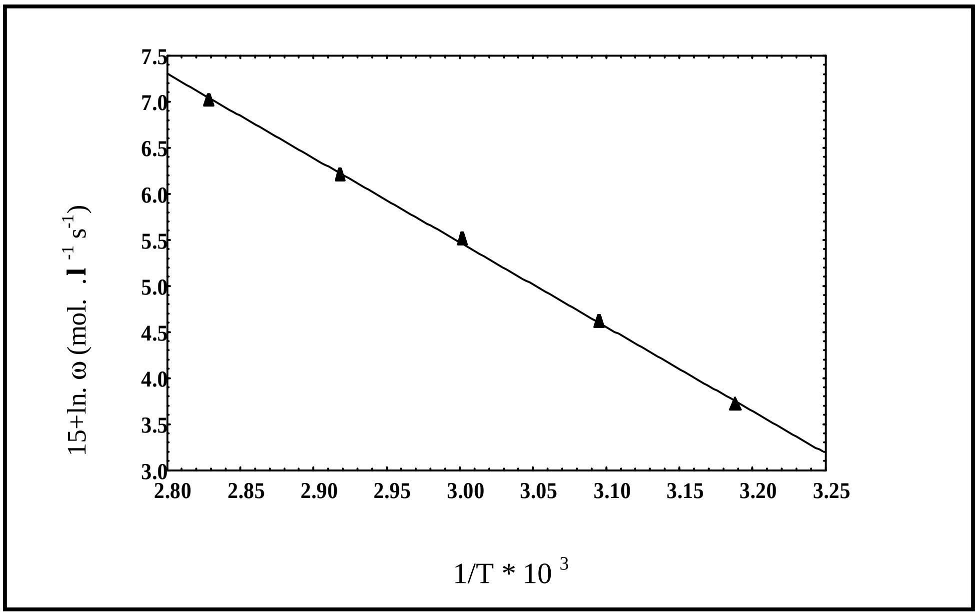


Fig.(5): Arrhenius plot of the rate of polymerization of MMA with reciprocal absolute temperature [VOL_2OCH_3]= 3×10^{-5} mol . l^{-1}.